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LETTER TO THE EDITOR

Near-threshold structure in the atomic K-shell spectra for ionisation by photons or fast charged particles†

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Abstract. Spectra of the optical and generalised oscillator strength for the K-shell ionisation of all free atoms with $Z \leq 30$ have been calculated within the framework of a Hartree–Slater central potential. One of our findings is that the spectra (at fixed small values of momentum transfer including the optical limit) are rich in structure, i.e. the spectral strength is non-monotonic in the kinetic energy of an ejected electron near the K threshold, for all atoms with $Z \geq 8$. This is in sharp contrast to the hydrogenic result, according to which the spectral strength for every shell monotonically decreases with the kinetic energy. The magnitude of the near-threshold structure sometimes amounts to 30%. A partial interpretation of the structure is given and consequences of these results to applications such as electron energy-loss spectroscopy and stopping-power calculations are pointed out.

The differential *optical* oscillator strength $df/d\epsilon$ for ionisation resulting in an ejected electron of kinetic energy ϵ is proportional to the photoionisation cross section (Fano and Cooper 1968). It has been known for some time (Manson 1976, 1977, Manson and Dill 1978) that $df/d\epsilon$ does not necessarily decrease monotonically with ϵ from the threshold for outer atomic subshells. The same is also true for the *generalised* oscillator strength $df(K, \epsilon)/d\epsilon$ for ionisation at monentum transfer $\hbar K$, when K is small. The quantity $df(K, \epsilon)/d\epsilon$ is the essential factor in the Born cross section for secondary-electron ejection by charged particles (Inokuti 1971) and it tends to $df/d\epsilon$ in the optical limit $K \to 0$. The non-monotonic ϵ dependence, or structure in the spectral strength, is related primarily to angular momentum barriers to the escape of electrons near the threshold (Fano and Cooper 1968, Fano 1972). These barriers are known to be especially important to continuum waves with angular momentum $l \geq 2$ near the outer edge of the atom. Thus, it has been thought that the K-shell ionisation should be unaffected by the barrier effect because the K-electron wavefunctions are quite compact and because the final state is limited to p waves only, by the dipole selection rule.

We have carried out comprehensive calculations of $df/d\epsilon$ and $df(K, \epsilon)/d\epsilon$ for the K shells of all atoms from Li ($Z = 3$) to Zn ($Z = 30$), employing Hartree–Slater wavefunctions (Herman and Skillman 1963) and methods earlier described in detail (Manson and Cooper 1968, Manson and Dill 1978, Manson 1976). As an example, results for Cu ($Z = 29$) are shown in figure 1(a), where it is seen that $df/d\epsilon$ is clearly

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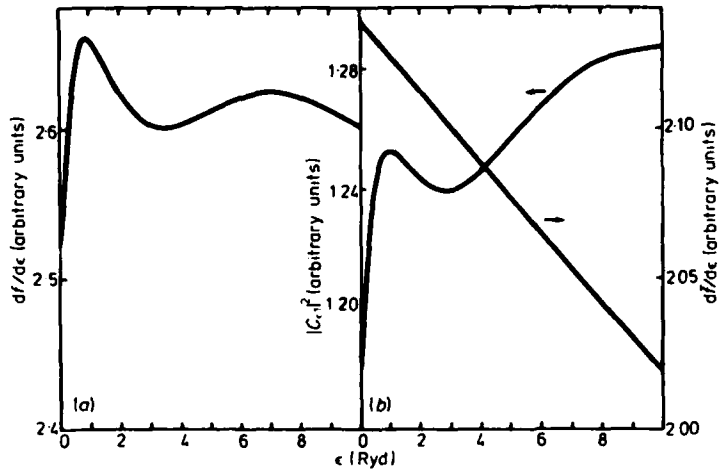

Figure 1. Cu K shell (*a*) $df/d\epsilon$; (*b*) $d\bar{f}/d\epsilon$ (right scale), $|C_{\epsilon 1}|^2$ (left scale). See text for an explanation of these quantities.

non-monotonic in ϵ, unlike the screened hydrogenic result (Hall 1936, Bethe 1933). In fact, the curve for $df/d\epsilon$ has two maxima, neither of which is at threshold.

To understand this behaviour, we use some of the ideas of the phase-amplitude method (Dehmer and Fano 1970, Fano *et al* 1976). In this method, the energy-normalised radial wavefunction $P_{\epsilon l}(r)$ for the electron of energy ϵ and angular momentum l is written as

$$P_{\epsilon l}(r) = \alpha(r)\,(f(r)\cos\delta(r) - g(r)\sin\delta(r)) \tag{1}$$

where $\alpha(r)$ is the amplitude function, $\delta(r)$ the phase function, $f(r)$ the regular Coulomb function, and $g(r)$ the irregular Coulomb function, all referring to the same ϵ and l. In this notation

$$df/d\epsilon = |\alpha_{\epsilon l}(0)|^2 B\, d\bar{f}/d\epsilon \tag{2}$$

where B is the square of the hydrogenic continuum wavefunction normalisation per unit energy (Seaton 1958, 1966) and $d\bar{f}/d\epsilon$ is a *reduced* oscillator strength density and should be slowly varying in ϵ, especially for inner-shell ionisation. In other words, the energy dependence of $df/d\epsilon$ is largely governed by $\alpha_{\epsilon l}(0)$ (B varies slowly), which reflects the potential seen by the escaping electron in the innermost region of the atom (Manson and Cooper 1968); indeed, $\alpha_{\epsilon l}(0)\,B^{1/2}$ is proportional to the coefficient $C_{\epsilon l}$ in the initial behaviour of the wavefunction,

$$P_{\epsilon l}(r) = C_{\epsilon l} r^{l+1}$$

at small distances r.

The two factors $C_{\epsilon 1}^2$ and $d\bar{f}/d\epsilon$ for the Cu K ionisation are shown in figure 1(*b*) for illustration of the ideas presented above. The reduced oscillator strength $d\bar{f}/d\epsilon$ is monotonically decreasing in ϵ, virtually in a straight line in the energy region which is tiny compared with the Cu K binding energy of about 649 Ryd. This behaviour of $d\bar{f}/d\epsilon$ is reminiscent of the screened hydrogenic result; indeed, the slope of $d\bar{f}/d\epsilon$ agrees closely with that result when the inner-screening constant is suitably chosen.

The other factor, $C_{\epsilon 1}^2$ varies sharply over the first ten rydbergs above the threshold. The variation is the origin of the structure in $df/d\epsilon$ and is another of the electron optical effects of atomic fields; a number of these are well understood (Fano and Cooper 1968, Manson and Cooper 1968). However, we have not fully delineated the details of this effect in the sense of Fano *et al* (1976).

The results for Cl ($Z = 17$) are shown in figure 2. Here again, $df/d\epsilon$ varies up and down (24%) near the threshold. The variation is entirely attributable to that in $C_{\epsilon 1}^2$, the reduced strength $d\bar{f}/d\epsilon$ monotonically decreasing in the same way as the screened hydrogenic result. However, Cl differs from Cu in details of finer structure (which we shall take up in a full paper in the future).

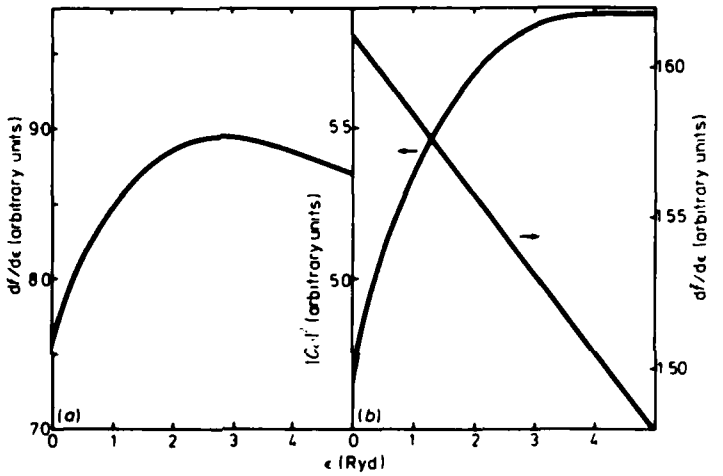

Figure 2. Cl K shell (*a*) $df/d\epsilon$; (*b*) $d\bar{f}/d\epsilon$ (right scale), $|C_{11}|^2$ (left scale). See text for an explanation of these quantities.

Now we stress that the near-threshold structure is common to many atoms and is not an isolated curiosity. Although we have presented here the results for Cu and Cl, we found, in fact, the presence of the near-threshold structure in all atoms with $8 \leq Z \leq 30$. Furthermore, the structure has an appreciable magnitude: 10% for Al ($Z = 13$), and 24% for Ar ($Z = 18$), for instance. Thus, we strongly suspect that it occurs for all atoms in the rest of the periodic table. (A realistic study of the heavier atoms requires taking into account the relativity effects and is being deferred for the present.) Finally, the generalised oscillator strength at small values of momentum transfer has essentially the same near-threshold structure as the optical oscillator strength.

There are several important implications of our results. First, in the study of solids by photoemission or electron energy-loss spectroscopy, one will often observe a near-threshold structure and might be tempted to attribute it immediately to solid-state effects. Certainly an electron escaping with a low kinetic energy has an ample opportunity to experience details of a non-isotropic potential due to chemical binding and solid-state effects; manifestations of such effects are exemplified by the Dehmer–Dill shape resonance (Dehmer and Dill 1975) and by the EXAFS. Yet, it is important to recognise that the free-atom spectral strength already has a near-threshold structure.

Second, when one calculates the K-shell ionisation cross section within the first Born approximation or attempts to improve upon it, it is necessary to use realistic $df(K, \epsilon)/d\epsilon$ values rather than the screened hydrogenic values. Especially for the spectra of secondary electrons with low kinetic energies, the hydrogenic results will be even qualitatively unrealistic. Finally, the use of realistic $df(K, E)/d\epsilon$ values may be important for evaluating the inner-shell correction to the Bethe stopping-power formula (Bethe and Ashkin 1953, Fano 1963).

In conclusion, we note that the use of wavefunctions which are more accurate than the Hartree–Slater wavefunctions is unlikely to alter our qualitative conclusions, as far as free atoms of lower Z elements are concerned. An improved calculation can be envisioned in terms of the Hartree–Fock method, including core relaxation effects, or an even more accurate method of configuration mixing. Either way, for the K shell, which has a large binding energy, the corrections to the Hartree–Slater result would have to come from virtual states of high energies and thus are unlikely to be appreciable.

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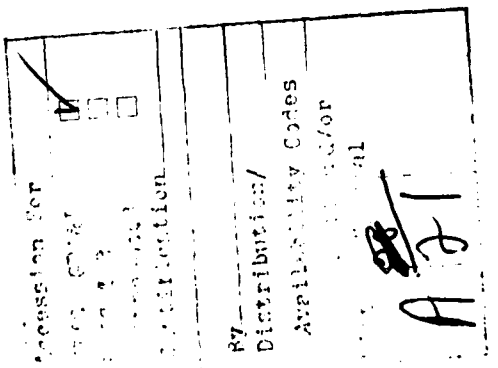

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